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Ab Initio Quantum Chemistry Calculations on the Electronic Structure of Heavier Alkyne Congeners: Diradical Character and Reactivity

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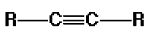
Abstract: The electronic structure of the heavier congeners of alkynes has been studied with emphasis on characterizing their extent of diradical character. Four orbitals play a crucial role in determining the electronic structure in planar trans-bent geometries. Two are associated with an out-of-plane π interaction, π and π^*, and two are associated with in-plane interactions and/or in-plane lone pairs, *LP*(n_-) and *LP**(n_+). The ordering of these orbitals can change depending upon geometry. One extreme, corresponding to the local minimum for Si−Si and Ge−Ge, is a diradicaloid multiple-bonding configuration where *LP* and π are nominally occupied. Another extreme, corresponding to a local minimum for Sn−Sn, is a relatively closed-shell single-bond configuration where *LP* and *LP** are nominally occupied. This ordering leads to predicted bond shortening upon excitation from singlet to triplet state. For the heavier elements, there appears to be very little energy penalty for large geometric distortions that convert from one ordering to the other on the singlet surface. The implications of these results with respect to experimental observations are discussed.

1. Introduction

The new millennium has witnessed the synthesis of the first stable examples of homonuclear alkyne analogues of the heavier main group 14 elements, which have the general formula REER (E = Si, Ge, Sn, Pb; R = bulky aryl or silyl ligand).[1−5] This work was, perhaps, stimulated in part by the preparation of $(\eta^5\text{-}C_5H_5)(CO)_2Mo{\equiv}GeC_6H_3\text{-}2,6(C_6H_2\text{-}2,4,6\text{-}Me_3)_2$[6] and $[RGaGaR]^{2-}$,[7] and the theoretical investigation of the latter species thereafter.[8−10] Single-crystal X-ray diffraction studies of the heavy group 14 element alkyne analogues revealed that their most striking feature is that they have a trans-bent, planar geometry instead of the familiar linear structure found for the lighter carbon homologue. In addition, the EE bonds are usually shortened relative to those in more highly coordinated compounds, but they are not as short as the triple bond lengths calculated for linear geometries.[11−16] The bending can be viewed as arising from accumulation of nonbonding electron density at the heavy elements and is accompanied by an apparent decrease in bond order on descending the group.[11−13] For the heaviest element, lead, the bond is essentially a single one, as shown by structure II.[1,14]



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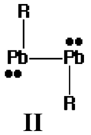

II

The element−element multiple bonds in the silicon, germanium, and tin analogues seem to lie between the extremes illustrated by structures I and II. Bond orders of ca. 2.4−2.6 have been calculated for silicon model compounds using the Wiberg[4] and Mayer bond order methods,[12] while a more recent topological analysis of the bond order predicted it to be approximately 2.[15] For the germanium model species MeGeGeMe, a bond order near 2.1 has been calculated from topological studies.[11,16] On the basis of the usual interpretation of results from the electron localization function (ELF), in which monosynaptic basins are regarded as nonbonding and disynaptic basins as bonding, silicon and germanium REER species (R = H or Me) were proposed to have a single E−E bond and two

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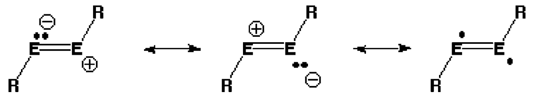
"lone pairs" on each E atom, to a first approximation.[11] However, those "lone pairs" extend significantly into the bonding region, and therefore it was concluded that the bond order is greater than 1 (but smaller than 3).[11] Qualitatively, this intermediate bond order was attributed to larger atomic size and smaller electronegativity for the heavier elements that leaves some fraction of the valence electrons as nonbonding.

In valence bond terms, the approximate double bonding in MeGeGeMe can be represented by the canonical forms III and IV, in which a nonbonding electron pair can resonate between positions at either germanium.[16] Furthermore, it has also been recognized that the bonding can involve contributions from the diradical form V.[11] The available spectroscopic data indicate that the trans-bent Si−Pb derivatives are diamagnetic, so that the diradical character of V, if it exists, must be of singlet type. Reactivity studies of the recently synthesized Ar′GeGeAr′ and its tin analogue Ar′SnSnAr′ (where Ar′ = Terphenyl)[17−19] indicate that the germanium compound is extremely reactive and that its reactivity is significantly greater than that of the tin analogue.[20] This is contrary to what is expected on the basis of steric effects and the bond strengths and polarities in the two compounds. We speculated that these differences might have their origin in greater diradical character of the germanium derivative.[20]



III **IV** **V**
(E = Ge)

Computational quantum chemistry methods are an attractive approach for understanding the structure and bonding in the heavier main group element analogous of alkynes, particularly given the challenges of experimental synthesis and characterization. It emerged quite early (indeed prior to the first experimental confirmation) that the heavier alkyne congeners behave quite differently from their carbon analogue. This is especially true for hydrogen derivatives where, because of hydrogen's bridging ability, structures featuring one[21] or two hydrogen bridges were calculated to be minima on the potential energy surface (PES). The existence of such structures was recognized in theoretical studies in 1982,[22] where it was also shown that the linear HSiSiH structure was the least stable of the isomeric forms considered. Subsequently, it was shown that linear structure is not even a minimum on the PES.[23−25] Instead, the nonplanar, doubly hydrogen-bridged isomer was found to be the global minimum with planar trans-bent structures as higher local minima.

The strong effect of the substituent at the group 14 element was emphasized by studies of Si_2R_2 (R = Me, SiH_3, $SiMe_3$, etc.), which showed that the bridged structures associated with Si_2H_2 were destabilized due to steric effects upon substitution and disappear from the potential energy surface as R becomes bulkier.[26,27] Of the four different structures considered, the vinylydene form (for example, $Me_2Si{=}Si$) had the lowest energy, and the trans-bent structure corresponded to the transient MeSiSiMe species observed in thermolysis reactions.[28] Chen et al. also showed from density functional theory (DFT) and Møller−Plesset (MP2) calculations of the lead species that, by changing the substituents from hydrogen to phenyl to 2,6-$Ph_2C_6H_3$, the trans-bent form becomes a true minimum due mainly to steric effects.[14]

The late 1980s and early 1990s saw additional computational studies of increasing sophistication.[29−31] In addition, increasing computing power permitted consideration of model species with larger substituents, leading to predictions that disilyne species exist with sufficient stability to be experimentally isolated.[26,27,32−34] Studies were also extended to include the heavier germanium, tin, and lead congeners, which behaved similarly to their silicon counterpart,[35−37] with a bent doubly bridged hydrogen structure being the global minimum. The relative energies of the isomeric forms change upon descending the group, with the existence of nonbonding lone pairs becoming a more prominent feature. In the most recent DFT calculations which support these conclusions, Lein et al. explained various isomers of HEEH (E = Si, Ge, Sn, Pb) and their relative stabilities in terms of doublet quartet energy differences of the EH fragment of HEEH,[38] whose utility in the context of a stable bridged HSiSiH isomer in comparison to the carbon analogue was first used by Kobayashi and Nagase.[26] The doublet quartet separations of the EH units in the heavier elements were found to be much greater than those of carbon.[14,26,27,38]

Despite numerous calculations on model species for these alkyne analogues, none has yet comprehensively addressed the question of the extent of diradical character in the bonding.[39] We now report computational studies of the model species MeEEMe (E = Si, Ge, Sn, Pb) and show that the silicon and germanium species are characterized by significant diradical character, whereas their tin and lead analogues possess this character to a much lesser extent. Furthermore, the bonding in the tin and lead compounds emerges as much richer than this simple caricature implies. We find very little energy penalty for substantial changes (up to 0.5 Å) in the bond length. However, there is a large change in diradical character and thus, potentially, a large change in reactivity with this change in bond length.

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Table 1. Structural Parameters for the Planar MeEEMe Species, Where E = Si, Ge, Sn, and Pb

species[a]		(E–E), Å	(E–E–C)°	$\langle S^2\rangle$[c]
Si	singlet (0)	2.14	128.4	0.00
	triplet (0[b])	2.34	109.6	2.01
Ge	singlet (0)	2.29	125.7	0.00
	triplet (0)	2.56	107.4	2.01
Sn	singlet (0)	3.06	100.0	0.94
	triplet (0)	2.98	103.8	2.01
Pb	singlet (1[b])	3.32	95.7	0.76
	triplet (1[b])	3.21	101.8	2.01

[a] Numbers in parentheses indicate the number of imaginary frequencies. [b] For the triplet Si species, there are two very small imaginary frequencies of 32 and 27 cm^{-1}. For Pb, the singlet species has an imaginary frequency of 157 cm^{-1}, and the triplet species has one of 224 cm^{-1}. [c] $\langle S^2\rangle$ is the expectation value for the square of the electronic spin for the Kohn−Sham reference wave function; for the singlets, substantial deviations from the nominal value of 0 hint at the presence of strong electron correlations and diradical character.

This paper is organized as follows. First, we introduce the model compounds used in this study and describe the structural features of the optimized singlet and triplet geometries with the help of orbital pictures. We then present the results of torsional potential energy surface scans that measure the strength of the multiple bonds and characterize the flatness of the energy surfaces. Orbital occupation number analysis and a discussion of the implications for diradical character then follow, with a particular focus on the germanium and tin species in light of recent reactivity experiments.[20] Finally we close with some conclusions.

2. Results

2.1. Singlet and Triplet Structures. The methyl-substituted species, MeEEMe (E = Si, Ge, Sn, Pb), has been used as a tractable model compound to investigate the E−E bonding. All geometry optimizations were performed using spin-unrestricted density functional theory (DFT) at the B3LYP/CRENBL* level[40,41] (unless otherwise noted) using the Q-Chem program.[42] CRENBL* is a large-core uncontracted effective core potential basis that describes the outer valence electrons of H as (4s), C and Si as (4s4p1d), and Ge, Sn, and Pb as (3s3p4d).

EE bond lengths and MeEE bending angles (for planar structures only) are summarized in Table 1. The general trends in bond lengths and bending angles are roughly consistent with numerous previous results with hydrogen or bulkier substituents that yielded trans-bent isomers.[11,13,14,26,38] The most noticeable feature, perhaps, is that there exists a discontinuity in trend between the Si and Ge versus Sn and Pb species. Specifically, the bond length jumps from 2.1−2.3 Å to 3.1−3.2 Å, and the bending angle changes from ∼125° to ∼100° on going from Ge to Sn. This is at least partly due to the relatively large and abrupt increase in covalent radius for Sn (1.40 Å) and Pb (1.45 Å) compared to Si (1.17 Å) and Ge (1.22 Å). The significant change in bending angles (∼125° versus ∼100°) can also be associated with a change in hybridization such that the Si and Ge species are closer to Lewis structure I, while the Sn and Pb species are closer to II. The tin−tin distance (3.06 Å) and the corresponding bending angle (100.0°) in this methyl-substituted model are markedly different from the experimental measurements (2.66 Å and 125°) with Ar = terphenyl, although the structures of the other elements appear to compare quite well between the methyl model and experimentally realized molecules: 2.06 Å, 137° (expt) versus 2.14 Å, 128° (calc) for Si; 2.29 Å, 129° (expt) versus 2.29 Å, 126° (calc) for Ge; and 3.19 Å, 94° (expt) versus 3.32 Å, 96° (calc) for Pb. We will address this discrepancy between the Sn model molecule and the experimental Sn molecule in detail in the Discussion section (although it is still possible that use of different substituents and/or changes in the level of theory might alter the character of the Sn−Sn bond from being single-bond-like toward the shorter experimentally observed one).

Another quite striking difference between the silicon and germanium versus tin and lead species lies in the triplet geometries. For Si and Ge, bond lengths in their triplet states are 0.27−0.30 Å longer than those in the singlet state, while for Sn and Pb, triplet bond lengths are 0.08−0.11 Å shorter than singlet distances. In particular, the latter is somewhat counterintuitive, since normally the triplet bond length is longer than the singlet counterpart due to reducing the bond order. To understand how the reverse result arises for the Sn and Pb compounds, we have examined the frontier orbitals, which were determined by spin-flip time-dependent density functional theory (SF-TDDFT) calculations.[43] SF-TDDFT calculations permit the singlet and triplet states in diradicaloid molecules to be described at a more uniform level of accuracy than with regular DFT, without the issue of spin-contamination that is clearly evident in the results of Table 1. For these calculations, the B3LYP functional was used.

Figure 1 shows isosurfaces of the HOMO−1, HOMO, LUMO, and LUMO+1 at singlet optimized geometries (from Table 1).[14] The HOMO−1 is a skewed in-plane π bond for Si, while it looks more like an in-plane nonbonding orbital for Ge. We denote this level as *LP*(n$_-$). For Si and Ge, the HOMO is an out-of-plane π bond, denoted as π_{out}. The LUMO is an in-plane counterpart of *LP*, denoted as *LP**(n$_+$), while the LUMO+1 is an antibonding counterpart of π_{out}, denoted as π_{out}*. For Sn and Pb, similar assignments can be made, except that the ordering of π_{out} and *LP** is switched and *LP* is visually just a lone pair.[14] This orbital picture suggests that the Si and Ge species have bond order of about 2.0 + α, where α is determined by the extent of the in-plane π overlap.[44] By contrast, the tin and lead species appear to have essentially a single bond, since the HOMO−1 and HOMO are both nonbonding orbitals, *LP* and *LP**.

SF-TDDFT calculations also revealed that, in triplet configurations, one of the paired electrons originally occupying the HOMO in the singlet configuration is promoted into the lowest unoccupied level. In order words, for the Si and Ge species, one of the π_{out} electrons is promoted to the *LP** level in the triplet state, reducing the bond order by 0.5, while for Sn and Pb, one of the *LP** electrons is promoted into the empty π_{out}

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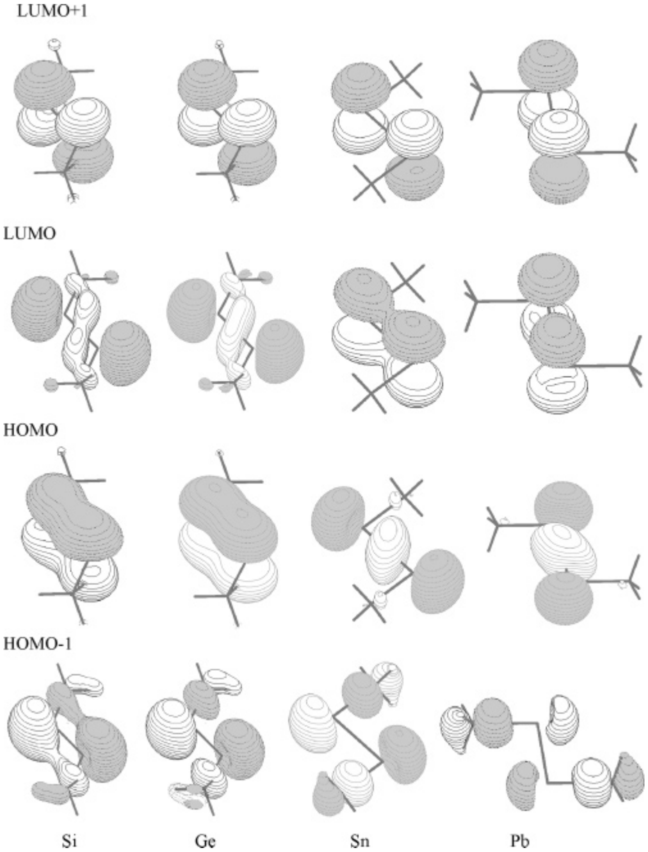

Figure 1. Frontier orbitals for MeEEMe (E = Si, Ge, Sn, Pb) model species determined from the triplet ground-state reference calculations in spin-flip (SF)-TDDFT to avoid spin-contamination.[43] In SF-TDDFT calculations, the ground state is taken as the triplet, and singlets are described as linear combinations of spin-flipping single excitations, which yields a description of singlet diradicaloid species that is nearly free of spin-contamination.

level, increasing the bond order by 0.5. As a result, for Si and Ge, the decreased bond order in the triplet state (changing from $2.0 + \alpha$ to $1.5 + \alpha$) makes the EE distance longer, while for Sn and Pb, the increased bond order (from 1.0 to 1.5) in the triplet is the origin of the shorter triplet EE distances.

Last, the trans-bending angles in the triplet geometries are all similar, ranging from ~102° to ~110°, with Sn and Pb having slightly sharper angles than Si and Ge (consistent with the above bond order prediction). This, together with the trend in the singlet geometries, hints that there may be a correlation between bending angle and bond order (or bond length). In other words, larger trans-bending angles are associated with stronger in-plane π-bonds, and thus larger overall bond order, and shorter bond lengths. In fact, this trend holds true for all four trans-bent systems (see Supporting Information for details).

2.2. Torsional Potential Energy Scans. We inferred from the structural and orbital analyses above that the (singlet) Si and Ge model species have bond order of $2.0 + \alpha$ (depending on the extent of trans-bending or the in-plane π overlap), and the Sn and Pb model species have bond order of approximately 1 (no π-bond). One straightforward way to measure the strength (and indeed the existence) of such π bond(s) is to compute the energy required to break them by twisting. We have obtained the relaxed potential energy curves for MeEEMe as a function of the C−E−E−C torsion angle (Figure 2)[45] by performing constrained optimizations at discrete values of the torsion angle (using conventional DFT with the B3LYP functional, as gradients are not yet available for SF-TDDFT). There are four main points that can be extracted from these torsion scans.

First, all four model species have surprisingly flat potential energy surfaces with respect to the torsion angle and associated bond length changes. For example, for tin, the increase in SnSn distance from 2.90 Å (gauche) to 3.06 Å (trans-bent) is accompanied by an energy increase of only ~2 kcal/mol, while for silicon, changing the SiSi bond length from 2.14 Å (trans-bent) to 2.48 Å (cis-bent) increases the energy by only ~10 kcal/mol. This is indeed quite intriguing because, in most molecules, significant changes in geometry and thus in the character of the wave functions will be accompanied by significant changes in energies.

Second, the gauche isomers are close in structure to the bridged configurations of HEEH, except that the positions of Me with respect to the two E atoms in MeEEMe are not symmetric. The bonded Me−E and "nonbonded" longer Me−E distances in the gauche form are 2.01 and 2.53 Å for Si, 2.10 and 2.68 Å for Ge, 2.35 and 2.96 Å for Sn, and 2.52 and 3.08 Å for Pb, respectively. Essentially, the scans in Figure 2 show that the "bridged" structures are more stable than the trans-bent structures by about 2−4 kcal/mol for Ge, Sn, and Pb. This is in sharp contrast to what was found in HEEH, where the "true" bridged structures were more stable than the trans-bent structures by 20−30 kcal/mol for all elements, E = Si, Ge, Sn, Pb.[38] The fact that the trans-bent singlet MePbPbMe is a saddle point (Table 1), while the trans-bent Ge and Sn species are true minima, can also be inferred from the dihedral scans shown in Figure 2.

Third, the tin and lead compounds require essentially no energy (<1 kcal/mol) to distort the planar structure to nonplanar (implying essentially no π bonding, consistent with the previous orbital picture), while the silicon and germanium molecules have 10 and 2 kcal/mol barrier heights for the distortion, respectively. Again, there is a clear contrast between two classes of molecule Si and Ge (that have some π bonding) versus Sn and Pb species (that have almost zero π bonding).

Fourth, for all elements, the planar cis conformation is higher in energy than the planar trans conformation. This may be due to additional repulsions between the co-facial E−C (in the E−Me moiety) σ bonds, and also between the lone pairs that are on the same side in the cis isomers.[38] It is also notable that the gauche isomers (~90° torsion angle) are more stable than the planar-trans conformations for the Ge, Sn, and Pb species.[38] This can be explained by a favorable donor−acceptor interaction between the E−C σ bond (which is donating some electron density) and the empty π orbital (which is accepting some electron density) across the E−E bond in the gauche conformation.[38] This emphasizes the necessity of employing bulky substituents to destabilize the gauche conformer through steric interactions if one wishes to experimentally isolate E−E bonds with the trans-bent geometry.

2.3. Diradical Character. Diradical character can be simply evaluated by computing the occupation numbers of antibonding orbitals.[46−48] However, antibonding orbitals are formally empty in conventional DFT calculations, and therefore wave function-based methods that include electron correlation are essential for this purpose. For this purpose, we employ inexpensive ap-

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(45) For readers' information, the torsional barrier for CH_3-CH_3 is ~3 kcal/mol, while that for $CH_2=CH_2$ is ~60 kcal/mol.

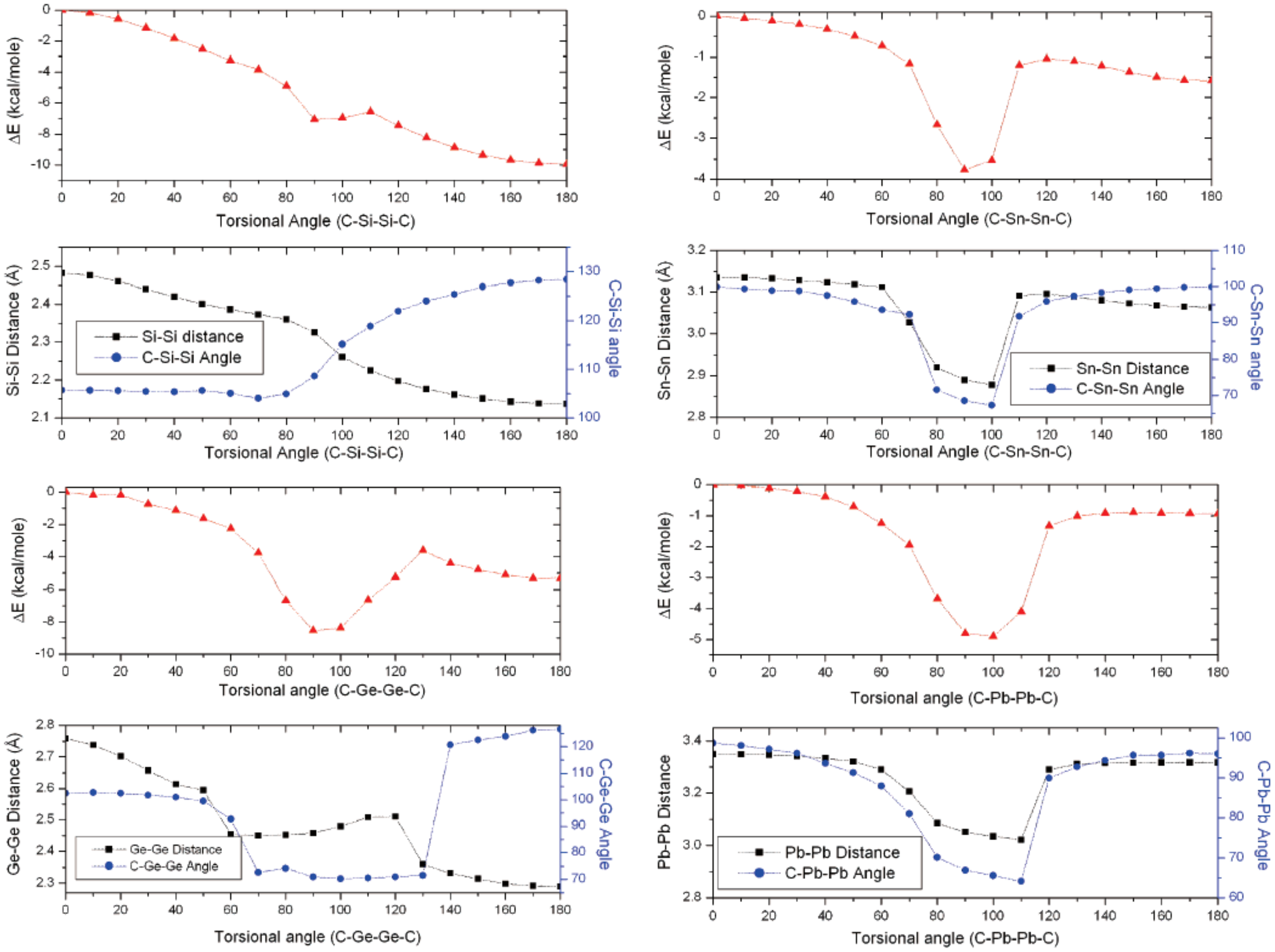

Figure 2. Fully relaxed potential energy scans for MeEEMe (E = Si, Ge, Sn, Pb) with respect to the C−E-E−C dihedral angle changes, computed via DFT with the B3LYP functional.

proximations to complete active-space self-consistent field calculations that allow all valence orbitals to be treated as active. Calculating the occupation numbers of antibonding orbitals via these inexpensive perfect-pairing (PP) or imperfect-pairing (IP) calculations[49−51] is an effective indicator of singlet diradicaloid character for diamagnetic molecules.[52,53]

Here we employ IP (to allow for potentially large correlations between the electron pairs associated with multiple bonding) to examine the diradicaloid character of the model MeEEMe systems. Two important correlations for the trans-bent multiple-bonded systems will be the *LP*-to-*LP** and π_{out}-to-π_{out}* correlations, whose extents are indicative of singlet diradical character since both correlations generate unpaired electrons localized on each E atom. It is, of course, possible that the IP correlated orbitals might be slightly (or even significantly!) different from the SF-TDDFT orbitals drawn in Figure 1. Therefore, we have plotted in Figure 3 the active IP pairs that have greater than 0.04 e^- "antibonding" occupation and summarized them in Table 2.

The Si and Ge species have strong π_{out}-to-π_{out}* and *LP*-to-*LP** correlations, yielding 0.11 and 0.17 unpaired electron, respectively, for Si and 0.13 and 0.13 unpaired electron for Ge. Such large "antibonding" occupations suggest quite strong diradicaloid character (and thus very high reactivity) in SiSi and GeGe multiple bonds. For comparison, CC in acetylene has 0.05 e^- antibonding π_x* and π_y* occupations, respectively. These occupation numbers may be multiplied by 100 and interpreted as the percentage of diradical character, consistent with 1 electron in the correlating orbital representing exact HOMO−LUMO degeneracy and thus a fully broken bond (100% diradicaloid).

In contrast, the Sn and Pb species have small "antibonding" occupations that are more similar to typical closed-shell molecules. For Sn, the largest correlations correspond to essentially atomic excitations (0.04 e^-), as seen in Figure 3, and the most active correlation in the case of Pb is σ-to-σ* excitation (0.08 e^-), both of which are probably due to the large EE distances in these model compounds. So, the correlation picture and corresponding occupation numbers for the methyl-substituted models clearly indicate that the silicon and germanium species have substantial diradical character while the tin and lead analogues are much less diradicaloid.

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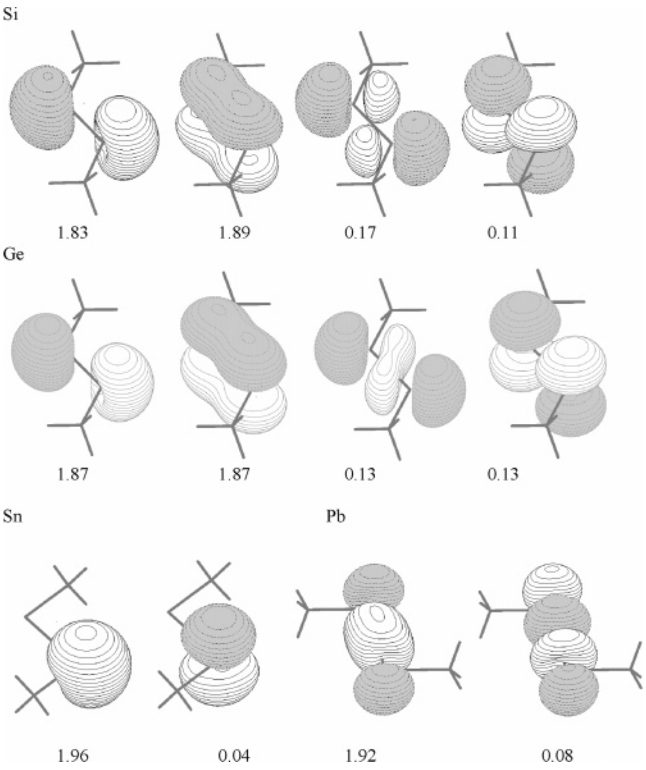

Figure 3. The most strongly correlated (diradicaloid) imperfect-pairing (IP) orbitals for MeEEMe (E = Si, Ge, Sn, Pb). For Sn, the correlated orbital pair essentially corresponds to an atomic excitation, and so for brevity, the same correlation but centered on the other Sn atom is not shown.

Table 2. Empty Level Occupation Numbers for the Most Strongly Correlated Active Pairs (with occupation greater than 0.04 e^-) for the MeEEMe Systems Obtained from Imperfect-Pairing (IP) Calculations Correlating All Valence Electrons[a]

	π_{out}-to-π_{out}*	*LP*-to-*LP**
Si	0.11 (0.12)	0.17 (0.17)
Ge	0.13 (0.14)	0.13 (0.15)
Sn	0.04 (0.05)[b]	0.04 (0.05)[b]
Pb		0.08 (−)[b]

[a] Numbers in parentheses correspond to occupation numbers with silyl substituents (silyl−EE−silyl) instead of methyl. For abbreviations, refer to the main text. [b] These correlations are not *LP*-to-*LP** or π_{out}-to-π_{out}* types. See Figure 3 for the corresponding orbital plots.

Table 3. Vertical and Adiabatic Singlet−Triplet Energy Gaps (in kcal/mol), Calculated Using Spin-Flip TDDFT[a]

	HOMO–LUMO	vertical gap	adiabatic gap
Si	−153.8	−32.4	−15.32
Ge	−148.3	−27.6	−11.54
Sn[b]	−99.3	−2.0	−1.25
Pb[b]	−94.2	−6.4	−6.19

[a] A negative sign means that the singlet is lower in energy than the triplet. HOMO−LUMO gaps (in kcal/mol) correlate well with S−T gaps. [a] Due to small HOMO−LUMO gaps for Sn and Pb, they have spin-unrestricted solutions. See also Table 1.

We have also calculated singlet−triplet (S−T) gaps, which are another signature of singlet diradical character. Adiabatic as well as vertical S−T gaps were calculated using SF-TDDFT, as summarized in Table 3, where the singlet was found to be the ground state for all elements. The silicon and germanium species have large S−T gaps, whereas tin and lead species show very small S−T gaps. This appears contradictory to the occupation number analysis described above, since smaller S−T gaps usually mean greater diradicaloid character. However, there is no inconsistency between these two analyses for the reasons that follow.

The lowest triplet configuration is achieved by promoting an electron from HOMO into LUMO (and flipping its spin), and therefore the HOMO−LUMO gap will roughly determine the promotion energy. The HOMO−LUMO gaps shown in Table 3 indeed agree well with the S−T gaps. However, such a HOMO-to-LUMO excitation *within the ground singlet-state wave function* for the Sn and Pb compounds is unlikely to occur because the LUMO is not the right correlating orbital for the HOMO (Figure 1). This is confirmed by a small expansion coefficient for this configuration in the multi-determinantal singlet wave function. Therefore, the small HOMO−LUMO gap (and thus the small S−T gaps) for the Sn and Pb species should not be directly translated as high diradical character in the ground-state singlet.

3. Discussion

As described in the Introduction, recent studies[20] of the reactivity of experimentally isolated molecules have uncovered some surprising results that are not easily accounted for in terms of current knowledge about the nature of bonding in the heavier alkyne congeners. Perhaps the most prominent of these is the fact that the germanium species ArGeGeAr (Ar = C_6H_3-2,6-(C_6H_3-2,6-$^iPr_2$)$_2$ (Ar′) or C_6H_3-2,6(C_6H_2-2,4,6-$^iPr_3$)$_2$ (Ar*)) display a much higher reactivity than their tin or lead counterparts. One possible explanation for this difference could be in the greater singlet diradical character of the germanium species, which is accordingly one of the central questions that this present study seeks to answer by computational studies on model compounds.

As described above, singlet diradical character of the germanium compound is associated with significant occupations of antibonding π_{out}* and *LP** orbitals. Because of the quite significant 0.13 e^- π_{out}* occupancy (about twice that of a conventional π bond), the π bond in MeGeGeMe, which is common in resonance structures III, IV, and V, is best described as a partial π bond (i.e., 87%) with some 13% diradical character.[54] The equally strong *LP*-to-*LP** correlation also makes the germanium compound diradicaloid, since it creates partially unpaired electrons on each Ge atom. In fact, this *LP*-to-*LP** correlation is responsible for the resonance structure V. Therefore, it can be said that the origin of diradicaloid character of the germanium species is a 13% diradicaloid π bond together with 13% diradical character in its partially unpaired nonbonding electrons. By contrast, the tin analogue in its singlet ground state is electronically closed-shell-like (i.e., 96% closed-shell character), and the “diradical character” (4%) due to “atomic excitations” is very small.

As mentioned in the previous section, the calculated structures of the silicon, germanium, and lead species with methyl substituents compare fairly well with the (different) experimentally realized species. By contrast, tin with a methyl substituent has a drastically different optimized geometry compared to experiments (3.06 Å and 100.0° for the Me model versus 2.66 Å and 125° for the synthesized molecule). The experimentally

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(54) For comparison, π_{out}* occupation of 0.13 e^- for germanium is greater than that for ethylene for the same type of correlation (0.07 e^-) but smaller than that of the extremely reactive dimer bond of the Si(100) surface, whose π* occupation is ~0.19 e^-.

Table 4. Comparative Occupation Numbers for the Germanium and Tin Species with Varying Substituents from the IP/CRENBL* Calculations, Including All Valence Electrons[a]

	$R = CH_3$	$R = SiH_3$	R = phenyl	R = Ar[d]
Ge[b]	0.13 e^-,0.13 e^-	0.14 e^-,0.15 e^-	0.15 e^-,0.17 e^-	0.14 e^-,0.18 e^-
Sn[c]	0.16 e^-,0.13 e^-	0.18 e^-,0.16 e^-	0.16 e^-,0.17 e^-	0.18 e^-,0.16 e^-

[a] The first entry in each column corresponds to the π_{out}* occupation number, and the second entry is the *LP** occupation. [b] For Ge, constraint-free optimization reproduced the experimental bond length and bending angle quite well, and those geometries were used in the IP calculations. [c] For Sn, constrained geometries with experimental bond length and bending angle have been used. [d] Occupation numbers for R = Ar were computed at the CASSCF(4,4)/HW(d) level due to the computational size of the system.

employed terphenyl substituent is certainly substantially bulkier and presumably more electropositive than methyl, and thus steric and/or electronic substituent effects could be responsible for this discrepancy. Electronic effects can arise from the fact that the phenyl rings directly attached to the tin (or germanium) atoms in the experimental structures are actually coplanar with the −PhEEPh− plane, allowing orbital interactions between the π system in the neighboring phenyl groups and the central EE π bond.

To investigate the role of substituent effects, we therefore performed constrained optimizations for the tin species with both bond length and bending angle constrained to the experimental values (2.66 Å and 125°), to mimic the geometric environment in the experimental molecule, while varying the substituents from methyl to silyl to phenyl to explore the electronic effects. The resulting orbitals (for all three substituents) indicate that the (relaxed) germanium and the (constrained) tin species show similar bonding pictures. Relative to the optimized geometry of the tin compound considered in the previous section, the wider bending angle and reduced bond length at the experimental geometry cause the ordering of orbitals for the tin species to change such that the π orbital becomes the HOMO.[55] Occupation numbers computed at the optimized geometries with these geometric constraints are summarized in Table 4. Electronic effects due to the different substituents appear to only slightly perturb the occupation numbers. Computed occupation numbers for the actual experimental molecules are also roughly consistent with the model compounds at the constrained geometry.

The results presented in Table 4 appear to be in contradiction with the recent reactivity experiments, since the calculated diradical characters of the germanium and tin compounds are similar, unlike the experimental observation, where the tin species is significantly less reactive. To address this puzzle, we recall from the previous section on torsional scans that substantial geometric changes in the model compounds can carry only modest energy penalties. Indeed, the energy penalty for changing the equilibrium structure (3.01 Å and 99.4°) for the silyl-substituted Sn model to the constrained one (2.66 Å and 125.0°) is only 3.8 kcal/mol. It is then conceivable that the experimental compound with the terphenyl substituent may also have a similarly small energy penalty associated with a substantial structural change.

In fact, in their theoretical prediction with the actual experimental substituents (i.e., Ar*), Takagi and Nagase reported that the elongated configuration (Sn−Sn = 3.05−3.09 Å) and the contracted one (Sn−Sn ≈ 2.66 Å) differ in energy by only 0.8−2.4 kcal/mol.[56,57] An energy difference of 0.8−2.4 kcal/mol is small enough that it could be altered by a small environmental perturbation to change the ordering of the two. Because the experimental structure was determined by X-ray diffraction, the structure measured is, to be precise, the tin compound under crystal packing forces, which are expected to be weak but might be sufficient to cause the solid-state structure to prefer an equilibrium geometry with shorter bond length.

Without the crystal packing force, and in the presence of solvent, perhaps Ar′SnSn′Ar might adopt the stretched form (Sn−Sn ≈ 3.05 Å), since it is the computed global minimum (or very close to it − within 0.8 kcal/mol).[56] Therefore, one possible resolution of the discrepancy between calculations and experiment is that the tin species observed in liquid-phase reactivity experiments has the elongated structure with Sn−Sn ≈ 3.05 Å, which is almost closed-shell-like and relatively unreactive, as we have shown with the model compounds. We are then led to speculate that, in the solid-state environment corresponding to the X-ray structure, the shorter bond length diradicaloid structure is preferred, perhaps due to crystal packing forces.

In other words, we suggest that the electronic structure of the tin species can vary quite significantly, depending on the environment, due to the quite flat nature of the potential energy surface. It can have bond order $2 + \alpha$ as in the germanium analogue, or it can be essentially a single bond as in lead, depending on the environment and the fact that the four important orbitals can change order with changes in bond length. We have already demonstrated that this can be the case with the results of the calculated torsional potentials discussed in the previous section and the small energy penalty demonstrated above for the imposition of geometric constraints corresponding to the experimental Sn−Sn geometry.

Contrasting results from reduction experiments on EGeGeE versus ESnSnE (where E is a terphenyl substituent, Ar′ or Ar*) appear consistent with this explanation. Power et al.[58] showed that adding one and then two electrons steadily increases the Ge−Ge distance for the germanium species. This is consistent with the LUMO being primarily lone pair in character, so that reduction increases the repulsion between electron densities around each Ge atom, which then lengthens the bond. For the tin compounds, adding one electron lengthens the Sn−Sn distance, but addition of the second electron then shortens the Sn−Sn bond length. The fact that addition of the second electron shortens the Sn−Sn bond length suggests that this electron fills a previously empty orbital that is partly bonding in character, which could be the π LUMO depicted in Figure 1. This is consistent with facile structural changes (and thus changes in

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(55) In other words, mixing of atomic p_z orbitals on each Sn that yields π_{out} and π_{out}* is stronger at a shorter SnSn distance, stabilizing π_{out} while destabilizing the π_{out}* level. Likewise, *LP** (which, at a longer bond length, was below the π_{out} level) is destabilized, and finally π_{out} becomes lower in energy than *LP** and occupied.

(56) Takagi, N.; Nagase, S. *Organometallics* **2001**, *20*, 5498.

(57) For ArSnSnAr, the computed conformation that is closer to the experimental structure with Sn−Sn = 2.66 Å is more stable than the singly bonded isomer with Sn−Sn = 3.09 Å by only 0.8 kcal/mol. For TbtSn−SnTbt (where Tbt = 2,4,6-tris(bis(trimethylsilyl)methyl)phenyl), the structure with Sn−Sn = 3.05 Å and Tbt−Sn−Sn = 97.3° is the global minimum and is more stable than the structure with Sn−Sn = 2.66 Å and Tbt−Sn−Sn = 122.0° by 2.4 kcal/mol (ref 56 and a private communication with the authors).

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the orbital ordering and reactivity) of the tin compounds in different environments, an idea which now awaits more definitive confirmation by higher level calculations and further experimental studies. It would constitute a fascinating form of bond-stretch isomerism induced by environmental perturbations.

4. Conclusions

Methyl-substituted model compounds were used to understand the electronic structure of the homonuclear alkyne analogues of group 14 elements, and they were found to capture many of the interesting features of experimentally isolated molecules with more complicated substituents. Our main conclusions are as follows:

1. For the singlet ground state at the computationally optimized trans-bent geometry, the silicon and germanium species are characterized by a partial out-of-plane π bond and a partial in-plane π bond that resembles the nonbonding lone pair to some degree, described by the orbital $LP(n_-)$. By contrast, the tin and lead species share a different bonding picture that is essentially a single bond with two pairs of nonbonding electrons (described by $LP(n_-)$ and $LP^*(n_+)$), due to a change in orbital ordering that leaves the π level empty.

2. For the lowest triplet state in the trans-bent geometry, the bond order of the silicon and germanium species is reduced by 0.5 due to an electron promotion from π to the empty π^* level. By contrast, the triplet bond order for tin and lead is increased by 0.5 due to an electron promotion from LP^* to the empty π level. Bond length changes from singlet to triplet support these bond order changes.

3. The calculated diradical characters of the trans-bent silicon and germanium species are found to be significantly higher than those of the tin and lead analogues, consistent with the recent reactivity experiments on the germanium and tin species, where the former was found to be substantially more reactive than the latter. The "out-of-plane π" bond and nonbonding (or "in-plane π") electron pair of the germanium species have about 15% diradical character associated with each, while the tin species has only about 4% diradical character, arising from the correlations that resemble atomic excitations.

4. The tin compound has an extremely flat potential energy surface, where the trans-bent minimum (Sn−Sn ≈ 3.05 Å) is more stable than a trans-bent geometry where bond length and angle are constrained at experimental values (Sn−Sn ≈ 2.66 Å) by only 1−4 kcal/mol.[56] Applying the crystal structure constraints, the Sn orbitals reorder such that diradical character increases to be comparable to the Ge value, inconsistent with the experimental reactivity difference. This apparent paradox can be resolved by hypothesizing, on the basis of the flatness of the potential surface, that crystal packing forces and/or solvent effects alter the bond length and thus the diradical character from solution to the solid state. This appears consistent with the results of reduction experiments.[58]

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Supporting Information Available: Complete ref 42 citation; table of structural parameters for the planar silyl-EE-silyl species (E = Si, Ge, Sn, and Pb); plots of potential energy versus C−E−E (E = Si, Ge, Sn, Pb) angle changes; and coordinates and energies (including $\langle S^2 \rangle$) of the structures summarized in Table 1 (both singlet and triplet), and also those of MeEEMe (E = Si, Ge, Sn, Pb) along the dihedral potential energy scans shown in Figure 2. This information is available free of charge via the Internet at http://pubs.acs.org.

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